

IN THE CLAIMS:

The presently pending claims, as previously presented and amended, are as follows:

1. (Previously Presented) In a mass spectrometer for analysis of secondary ions and post-ionized neutral secondary particles comprising (a) an ion source to create a primary ion beam to irradiate a sample and create secondary particles, said source possessing a heatable ion emitter that is coated in the area exposed to the field with a liquid-metal layer that contains an ionizable metal that is emitted and ionized as the primary ion beam, wherein the primary ion beam contains metal ions with various stages of ionization and cluster statuses, and (b) a spectrometer unit for mass analysis of the secondary particles, the improvement wherein the liquid metal layer is essentially comprised of pure metallic Bismuth or of a low-melting-point alloy containing, in essence, Bismuth; wherein the ion emitter is wettable by such pure metallic Bismuth or such Bismuth alloy; wherein a Bismuth ion mixed beam can be emitted by the ion emitter under the influence of an

electric field and from which Bismuth ion mixed beam, one of a number of Bismuth ion types, whose mass is a multiple of monatomic singly or multiply charged Bismuth ions  $\text{Bi}_1^{p+}$ , is to be filtered out, using a filtering device, as a mass-pure ion beam that is solely comprised of ions of a type  $\text{Bi}_n^{p+}$ , in which  $n \geq 2$  and  $p \geq 1$ , and  $n$  and  $p$  are each a natural number;

thereby to increase the efficiency of secondary ion production from the sample, relative to bombardment of the sample with  $\text{Au}_1^+$  gold ions.

2. (Previously Presented) Mass spectrometer as in Claim 1, wherein the ions filtered out for a mass-pure ion beam belong to one of the following types:  $\text{Bi}_2^+$ ,  $\text{Bi}_3^+$ ,  $\text{Bi}_3^{2+}$ ,  $\text{Bi}_4^+$ ,  $\text{Bi}_5^+$ ,  $\text{Bi}_6^+$ ,  $\text{Bi}_5^{2+}$ , or  $\text{Bi}_7^{2+}$ .

3. (Previously Presented) Mass spectrometer as in Claim 1, wherein the secondary ion mass spectrometer may be operated as a flight-time secondary-ion mass spectrometer.

4. (Previously Presented) Mass spectrometer as in Claim 1, wherein the emission current of the primary-ion beam during operation is between  $10^{-8}$  and  $5 \times 10^{-5}$  A.

5. (Previously Presented) Mass spectrometer as in Claim 1, wherein a metallic alloy of Bismuth comprises Bismuth and a metal selected from the group consisting of Ni, Ag, Pb, Hg, Cu, Sn, and Zn, whereby an alloy is preferably selected whose melting point lies below that of pure Bismuth.

6. (Previously Presented) In an ion source to create a primary ion beam to irradiate a sample, and to create secondary particles for a mass spectrometer for analysis of secondary ions and post-ionized neutral secondary particles, said source possessing a heatable ion emitter that is coated in the area exposed to the field with a liquid-metal layer that contains an ionizable metal that is emitted and ionized as the primary ion beam, wherein the primary ion beam contains metal ions with various stages of ionization and cluster statuses, the improvement wherein the liquid metal layer is essentially comprised of pure metallic Bismuth or of a low-melting-point alloy containing Bismuth; wherein the ion emitter is wettable by such pure metallic Bismuth or such Bismuth alloy; wherein a Bismuth ion mixed beam can be emitted by the ion emitter under the influence of an electric field, from which Bismuth ion mixed beam, one of a number of Bismuth ion types whose mass is a multiple of

monatomic singly or multiply charged bismuth ions  $\text{Bi}_1^{p+}$ , is to be filtered out, using a filtering device, as a mass-pure ion beam that is solely comprised of ions of a type  $\text{Bi}_n^{p+}$ , in which  $n \geq 2$  and  $p \geq 1$ , and  $n$  and  $p$  are each a natural number;

thereby to increase the efficiency of secondary ion production from the sample, relative to bombardment of the sample with  $\text{Au}_1^+$  gold ions.

7. (Previously Presented) Ion source as in Claim 6, wherein the metallic alloy of Bismuth is coated with one or more metals selected from the group consisting of Ni, Ag, Pb, Hg, Cu, Sn, or Zn, and wherein an alloy is preferably selected whose melting point lies below that of pure Bismuth.

$n \geq 2$  (i.e. a cluster) and  $p \geq 1$  (i.e. cluster of charged Bismuth ions). Further, in claims 1 and 6, it is defined that the efficiency of secondary ion production from the sample is increased over the efficiency of  $Au_1^+$  gold ions.

In the present invention, Bi ion clusters are directly used in SIMS for sputtering a target to be analyzed. This use of the primary ion beam is different to the use of primary ion beams in MALDI (matrix assisted laser desorption and ionization), wherein a laser beam is used for generation of secondary ions. In MALDI, a primary ion beam may be employed to implant ions into the target matrix thereby modifying the chemical characteristics of the target and improving laser ionization/desorption of target material. Thus, SIMS and MALDI are different technologies.

In claim 1, the term "efficiency of secondary ion production from the sample" characterizes the ratio between the amount of generated secondary ions and consumed target/sample material. With the invention this efficiency is improved by using mass pure Bi ion clusters as primary ions over  $Au_1^+$  gold ions as primary ions.

## 2. General Background Information

As general information for understanding the present invention, the following provides a brief introduction to the state of the art at the time the invention was made:

At the time of filing, the priority date of August 25, 2003, it was the state of the art to use clusters like  $\text{Au}_2$  and  $\text{Au}_3$  to increase efficiency over  $\text{Au}_1$ . This has already been acknowledged on page 2, first paragraph, of the applicants' specification. However, there is no evidence of the use of other metal clusters in SIMS to increase the efficiency of secondary ion generation.

There had been reports on ions (molecules, organic clusters) with lower mass, e.g.  $\text{SF}_3$ ,  $\text{C}_n\text{H}_m$ , and higher mass, e.g.  $\text{C}_{60}$ , which showed efficiencies similar or higher than Au gold clusters. However, there was no report about higher efficiencies correlating with the mass of constituents if clusters were used.

The reason is that the generation of secondary ions by the sputtering of organic materials with primary ions is not as simple as is assumed by the Examiner. Not only is it necessary to take into account the energy transfer by the collisions, but also the chemical environment (matrix

effect) and its modification by the implanted primary ions. However, the interaction of organic materials with energetic cluster projectiles is not well understood and there are no rules that allow a prediction or extrapolation of the efficiency for a certain primary cluster based on the mass of its constituents, the number of constituents, and its total mass or ion charge. It is further not sufficient to evaluate the moderate differences in sputter yields. The ionization effects are by far more important, and these are not predictable in any way.

In addition, the performance of a cluster ion source (beam intensity, spot size) depends not only on the intensity of the different cluster species emitted but also on their energy distribution, their angular distribution and their virtual source size.

In late 1970's, there were studies by Orloff and others on liquid metal ion sources comprising Bi. These researchers were interested in the basic emission characteristics of such liquid metal ion sources and measured the whole emitted ion beam without mass filtering: i.e., a mixture of atomic ions and clusters with different numbers of atoms and different charge states.

Van de Walle and others measured the mass spectrum of Bi and found some Bi cluster ions with substantial intensities.

None of these groups involved in basic research on liquid metal ion sources gave any indication of, or hint for the use of such Bi cluster beams, not to mention their use in SIMS.

In particular, a person skilled in the art at the time of filing this application did not consider use of a Bi cluster source in SIMS for the following reasons:

1. Au (gold) was the de facto standard in SIMS as ion source.
2. It was not known whether Bi, compared to Au, had any beneficial or detrimental matrix effect due to its different chemistry, thereby influencing efficiency of secondary ion production.
3. The angle distribution of a Bi cluster ion beam was not known, nor was it known whether such a beam would have a sufficiently small focus on the target.

To summarize, at the time of filing this application, there existed some studies on the general characteristics of Bi liquid metal ion source. But there existed no information about the suitability of such ion sources in SIMS. Some relevant parameters, i.e. angle distribution,



matrix effect and chemistry of mass pure Bi clusters, were even not known at all.

### 3. Prior Art References

#### 3.1 Hamza et al.

Hamza et al. discloses a SIMS using an EBIT (electron beam ion trap) primary ion source followed by a mass filtering device. Such EBIT ion sources generate slow, highly charged ions (HCI), e.g.  $\text{Xe}^{44+}$ ,  $\text{Au}^{69+}$ . Such HCI have a very high potential energy but only a very low kinetic energy. Relevant for the high potential energy is the charge of the projectile, not its mass. EBIT sources thus effect an electronic sputtering of the target surface. An EBIT source as used in Hamza et al. cannot generate cluster ions at a high charge state as such cluster ions would undergo Coulomb explosion/repulsion. Hence, Hamza et al. cannot and does not teach the use of cluster ions.

Liquid ion sources as used in the present invention do not generate ions with high potential energy (i.e. high charge status) but only cluster ions with a charge state of +1 to +3. As mentioned above, it is impossible to generate clusters with very high charge states as they would undergo

Coulomb explosion. However, in such charged clusters, kinetic energy is dominant. Liquid ion source cluster primary beams sputter the target by an elastic collision cascade, which is a completely different physical and chemical process than electronic sputtering by EBIT sources.

Thus, Hamza et al. teach a technique (EBIT) which is totally different than a liquid metal ion source using clusters.

To summarize, Hamza et al.

- Does not teach a liquid metal source,
- Does not teach charged cluster ions,
- Does not teach cluster ions of low charge state,
- Does not teach the use as primary ion beam of projectiles for elastic cascade sputtering, and
- Teaches away from the invention to use an EBIT ion source with totally different characteristics.

A person skilled in the art who is looking for an improvement in efficiency of secondary ion generation over the de facto standard Au in SIMS would not be motivated to consult Hamza et al. Even if he did, he would be led away to use an EBIT ion source which does not generate cluster ions.

### 3.2 Schultz et al.

Schultz et al. discloses a MALDI mass spectrometer, wherein secondary ions are generated via laser desorption. This laser desorption is assisted by the matrix of the target to be sputtered. Schultz et al. now proposes to implant ionized clusters (Au, Al) from a liquid metal source into the matrix (near surface region) of the target in order to enhance laser desorption.

Schultz et al. is not at all concerned with sputtering a target by a primary ion source. The ion source in Schultz et al. is for implanting ions into the matrix as optical absorption sites for the laser light desorption.

Schultz et al. cannot modify Hamza et al. as their teachings concern totally different sputtering techniques. Even if these two references could be combined, the EBIT source in Hamza et al. would be replaced by the MALDI technology in Schultz et al.

Schulz et al. in fact discloses, for the ion implantation into the matrix, that laser desorption of ions from matrices which were modified by implantation of ions enhances the ion signal. However, Schultz et al. do not provide any information on target consumption. In contrast

to the opinion of the Examiner, Schultz et al. does not disclose that the efficiency of ion generation increases with mass of the implanted primary ion.

To summarize, Schultz et al.

- concerns a totally different technology (MALDI) than Hamza et al. (EBIT, SIMS),
- uses an assistive ion beam not as primary ion beam for sputtering but for matrix modification by ion implantation;
- concerns a different technology (MALDI), generating ions to be analyzed by laser desorption, than the present invention (SIMS) generating ions to be analyzed by sputtering with a primary ion beam;
- does not show higher efficiency for higher mass of implanted ions;
- does not show any beneficial effect on efficiency by higher mass of sputtering primary ions; and
- does not show Bi clusters.

A person skilled in the art and looking for an improvement in efficiency of secondary ion generation over the de facto standard Au in SIMS would not at all consult Schultz et al. Even if he did, he would not be lead away to use MALDI technology instead of SIMS because the effect of

matrix modification by implantation of metal ions would not teach him anything about the effects of specific ions as primary sputtering ion beam in SIMS.

### 3.3 Orloff et al.

According to the Examiner, Orloff et al. teach the use of a Bi liquid metal ion source for producing high current, medium energy Bi ion beams.

In fact, Orloff et al. teach a liquid metal ion source for use in surface analysis using an electrostatic lens system. They do not mention SIMS technology.

According to Orloff et al., the energy spread  $\Delta E$  of the primary ion beam is highly relevant for achieving a well focused beam spot for analysis. Orloff et al. discloses the use of a Ga liquid metal source together with his specific lens system.

Throughout this document, Orloff et al. use a Ga liquid metal ion source with an energy spread at optimum condition of 5.3 eV. Ga has a mass of 69 u and a melting temperature of  $T = 303$  K.

In contrast, Bi has a much higher mass ( $m = 209$  u) and a much higher melting temperature ( $T = 544$  K).

As the energy spread and thus focusability of a liquid metal source depends proportionally to the mass of the ion and the temperature of the liquid metal, Bi has serious disadvantages over Ga for use in surface analysis.

Thus, Orloff et al., which is most concerned with small target spot areas, certainly would suggest using Ga liquid metal ion sources instead of a Bi liquid metal ion source.

The statement in col. 10, l. 16, that liquid Bismuth generates results "entirely analogous to the results described before", refers to the electrostatic optical system developed and described by Orloff et al. suitable to focus ion beams. By no means can this phrase be understood such that Bi would provide beam parameters (energy spread, spot size, efficiency etc.) as good as a Ga ion source. This is not the case.

Orloff et al. therefore fails to teach:

- using a Bi liquid metal ion source in SIMS;
- using clusters as primary ions;
- using a filter to generate a mass pure primary ion beam;

- that Bi clusters according to the invention are superior over  $Au_1^+$  in efficiency of secondary ion generation.

To summarize, Orloff et al. would not guide a person skilled in the art who knows about the energy spread and spot size of Ga and Bi, to use mass pure Bi clusters in SIMS. Orloff et al. do not provide any teaching on the composition and characteristics of different species in a Bi beam emitted from a Bi liquid metal ion source.

#### 3.4 Liebl et al. (US 3,508,045)

The Examiner purports that Liebl et al. disclose that the mass of primary ions in SIMS should be as large as possible.

This document in fact refers to SIMS. Liebl et al. improves the sensitivity of SIMS by using chemically highly reactive ions, e.g. ions of high electronegativity as primary ions. Fig. 7 discloses that the relative ion yield increases with electronegativity of the ion. A comparison with Ar and Xe in Fig. 7 shows that - in contrast to the Examiner's statement - it is the greater chemical reactivity (higher electronegativity), and not the larger mass of the

primary ion, which leads to higher secondary ion yield.

Thus, Liebl et al. confirm that the chemical characteristics is much more relevant than the mass of the primary ion.

Bi has a lower electronegativity than Au. According to the teaching of Liebl et al., no improvement of ion yield would be expected or could be anticipated by replacing Au with the inventive Bi-clusters of lower electronegativity.

Taking Liebl et al. into account, a person skilled in the art would have rather used iodine clusters instead of Au as a primary sputtering ion beam in order to improve secondary ion yield.

Further, the contention of the Examiner that Liebl et al. show an enhancement of efficiency of secondary ion generation with mass of the primary ion is not entirely correct. In fact, with higher mass, the consumed target increases in parallel with the secondary ions. Hence, the efficiency does not change. Again, it must be stressed that it is mainly the chemical characteristics of primary ions which make them suitable for SIMS. However, this has neither been described nor suggested for Bi-cluster ions.

To summarize, Liebl et al. again guide the person skilled in the art away from the present invention. Liebl



et al. suggest using primary ions with high electronegativity rather than increasing the mass of the primary projectile.

Liebl et al. certainly constitutes proof for the fact that secondary ion generation in a target depends much more on the chemistry of the primary ion than on features like mass and charge state.

Thus, Liebl et al.:

- does not disclose or suggest a liquid metal ion source;
- does not disclose or suggest uses of Bi as ion source;
- does not disclose or suggest use of mass pure Bi-clusters in SIMS;
- suggest using highly electronegative ions as primary ions;
- confirms the importance of the chemical characteristics of a primary ion for high secondary ion yield; and
- does not disclose any advantage of a higher mass of primary ions for efficiency of secondary ion production.

Attached to this Response is a document prepared by the applicants and entitled "Comments to the Rejection of the United States Patent and Trademark Office". The Examiner is